

Occupational Exposure and Drift Hazard During Aerial Application of Paraquat to Cotton

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Abstract. Two worker-exposure and drift trials were conducted during the aerial application of paraquat to cotton in California, USA. The dermal and respiratory exposure of pilots, flaggers, and a mixer-loader was shown to be low. Dermal exposure ranged from 0.05 (pilot) to 2.39 (flagger) mg/hr. The dermal exposure of the mixer-loader was similar to that of the pilots. No respirable paraquat was detected in the breathing zone of any worker. The highest total paraquat concentration was 26.3 $\mu\text{g}/\text{m}^3$ for a flagger, which is a factor of 19 less than the TLV for total paraquat. The combined dermal and respiratory exposure of this flagger was equivalent to 19.4 mg/8hr working day. Paraquat drift concentrations decreased with increasing distance downwind of the spray application. The highest concentrations of total and respirable paraquat were 16.7 and 0.15 $\mu\text{g}/\text{m}^3$ at 50 m from the application site perimeter. The respective concentrations at 1600 m downwind were 0.5 and 0.01 $\mu\text{g}/\text{m}^3$. Measurement of the particle size distribution of paraquat drift showed that 0.95 to 1.96% of spray droplets was within the respirable range at all distances downwind. The highest percentage of respirable droplets was equivalent to 1.2 μg paraquat, which was measured at 400 m downwind. Respirable fractions of 1 and 0.95% were measured at 50 and 100 m downwind, which represented 1.8 μg paraquat. There was no evidence, therefore, of a toxic hazard to pilots, ground crew, and downwind bystanders, as a consequence of the aerial application of paraquat.

Paraquat, as Ortho Paraquat Cl[®] (1, 1-dimethyl-4, 4'-bipyridinium dichloride) containing 21.1% by weight paraquat ion, is a broad spectrum herbicide which is frequently applied aerially in the USA as a harvest aid for cotton defoliation. Previous studies of occupational exposure to paraquat have concentrated on workers using knapsack, hand-held pressurized, and tractor-mounted sprayers (Swan 1969; Hogarty 1975; Chester and Woollen 1982; Staiff *et al* 1975 and Wojeck *et al* 1983). Akesson *et al* (1977) and Seiber and Woodrow (1981) investigated the drift of paraquat during aerial application. In the present study, measurements were made of the potential dermal and respiratory exposure of workers, and downwind drift, during aerial application of paraquat for cotton harvest aid by commercial applicators. The San Joaquin Valley of California, USA was chosen for this study, because large quantities of paraquat are applied aerially in this area and, therefore, provided a typical use pattern and ideal conditions for this type of study.

Materials and Methods

Worker Exposure Studies

The subjects of the two exposure studies were two male pilots, two female flaggers (i.e., swath-markers) and one male mixer-loader, who were employed by Telles Ranch Inc, Firebaugh, Fresno, CA, who operated their own crop-spraying aircraft. The pilots were not issued with, nor did they wear, protective clothing. Their normal clothing consisted of open-necked, short-sleeved shirt, T-shirt, long trousers, boots and hat. The flaggers were issued with protective cotton overalls. The mixer-loader wore coveralls and rubber gauntlets and boots. No respiratory or eye protection was provided for, or worn by any worker.

Dermal exposure was measured by procedures based on those

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Table 1. Location of Exposure Pads

Pilots	Flaggers	Mixer-Loader
Forehead	Forehead (2nd trial only)	Forehead
Back of neck	Left shoulder	Back of neck
"v" of neck	Right shoulder	"v" of neck
Left forearm	Back of neck	Left upper arm
Right thigh	Abdomen (over chest)	Right thigh
Right lower leg	Left forearm	
	Left or right thigh	
	Left or right lower leg	

described by Durham and Wolfe (1962). Dermal exposure pads, consisting of polythene-backed 100 cm² Whatman 542 filter papers were attached to skin or clothing, using adhesive tape, at the positions shown in Table 1. The dermal exposure of the hands of the pilots and flaggers was measured by the use of bleached cotton gloves. Penetration of paraquat through clothing and protective clothing was assessed with white cotton T-shirts over the trunk, and cotton Tubigrips® (elasticated support bandages manufactured by Seton, Tubiton House, Oldham, England) located on the left leg (ankle to top of thigh) of each worker. All sampling media were worn for the duration of the aerial spraying procedures. They were then carefully removed avoiding accidental contamination, and placed in individual, labelled polythene envelopes and stored in the dark until analysis for paraquat content. Airborne concentrations of total (all droplets irrespective of size) and respirable (particle size diameters <7 µm) paraquat in the breathing zones of all workers were determined with Rotheroe-Mitchell (Greenford, Middlesex, England) L2SF® personal air samplers. For total paraquat determinations, the instruments were operated at a flow rate of 3 or 3.5 L/min for the duration of each trial, using Whatman Number 1 filters located in open sampling heads attached to the collars of the workers. In order to collect the respirable fraction, a flow rate of 1.9 L/min was required, and respirable droplets were collected on Whatman 542 filters located in Rotheroe-Mitchell mini-cyclones attached to the collars of the workers. Instrument flow rates were calibrated before and after each trial, using a Gap® (G A Platon Ltd, Basingstoke, Hampshire, England) flowmeter with a range of 0 to 5 L air/min. Both types of filter paper have collection efficiencies of 100% for particle sizes down to 2 µm diameter. 3M (3M Co, St Paul, MN) disposable filter facemasks were worn by the two flaggers throughout the second trial to provide an additional estimate of respiratory exposure. After each trial, all sampler filters and masks were removed with care to avoid accidental contamination, and stored individually in labelled sample tins before analysis for paraquat content.

Paraquat Drift Measurement

Rationale: The drift sampling method was similar to that described by Yates *et al* (1966 and 1974); they collected airborne and fallout samples at stations located 100 to 5000 ft downwind in a straight line. Their measurements were taken with a single swath which was repeatedly sprayed during specifically chosen

low wind velocity periods with constant wind direction. Our method differed only in that measurements of paraquat drift were taken during actual aerial application to a large acreage of cotton, in which the distance of the emitted spray to the field perimeter ranged from 0 to 1600 m (length of cotton field). Therefore, the distance of the spray, on emission, to the sampling stations varied according to where the aircraft was at any point in time. It was recognized that this method could give rise to variable results if a significant variation in wind direction occurred during the trials.

Procedure: Drift sampling stations were located on a center line downwind of each of the two spray applications. Careful observations were made of the prevailing wind direction on three days prior to the trials, and immediately before the stations were set up. The locations were 50, 100, 200, 400, 800 and 1600 m from the perimeter of the test sites (Figure 1). For the first trial, the following air sampling instruments were positioned at head height on a dais at sampling stations 1–5:

1. Staplex (Staplex Inc, Brooklyn, NY) Hi-Vol with TFA41 filter and operated at 425–453 L/min.
2. Staplex Hi-Vol with attached Andersen 2000 (Andersen 2000 Inc, Atlanta, GA) High Volume Particle Sizing Sampler operated at 481–590 L/min.
3. Casella (C F Casella Co Ltd, London, England) Hexhlet® with Whatman GF/A filter and operated at 50 L/min.

Since only five Hexhlets® were available, Station 6 (1600 m) consisted of a Staplex Hi-Vol, and Staplex plus Andersen particle sizer only. For the second trial, no station was set up at 200 m, as a Staplex Hi-Vol and Staplex plus Andersen particle sizer were located at head height in the vicinity of the mixing-loading operation on the downwind side. The Hexhlets® were used at all five remaining stations. Electrical power for the samplers was provided by portable 220 and 110v generators.

The functions of the three instruments were:

1. Staplex Hi-Vol—to collect all paraquat droplets of particle diameter 0.01 µm upwards.
2. Casella Hexhlet®—to collect respirable paraquat fraction droplets <7 µm diameter. The collection characteristics of the instrument are in accordance with the Johannesburg Conference curve (Orenstein 1960).
3. Staplex Hi-Vol with Andersen Particle Sizer—to collect and classify paraquat aerosol droplets into five fractions: <1.1 µm, 1.1–2.0 µm, 2.0–3.3 µm, 3.3–7.0 µm and >7 µm. These size categories simulate the collection characteristics of the human respiratory system in the following manner (Andersen 2000 Inc 1976):

Droplets >7 µm	—retained by nasal passages
Droplets 3.3–7.0 µm	—retained by trachea and primary bronchi
Droplets 2.0–3.3 µm	—retained by secondary bronchi
Droplets 1.1–2.0 µm	—retained by terminal bronchi
Droplets <1.1 µm	—retained by alveoli

The Andersen Particle Sizers were calibrated before and after each trial, by measurement of the pressure-drop across the sampling head, and comparison with standard calibration curves of pressure drop vs altitude at 560 L/min. The Staplex Hi-Vol and Hexhlet® samplers were calibrated after the completion of the trials. The sampling periods were from the time spraying commenced until 30 min after spraying ceased. This 30 min excess period was chosen to sample residual airborne paraquat drift. In

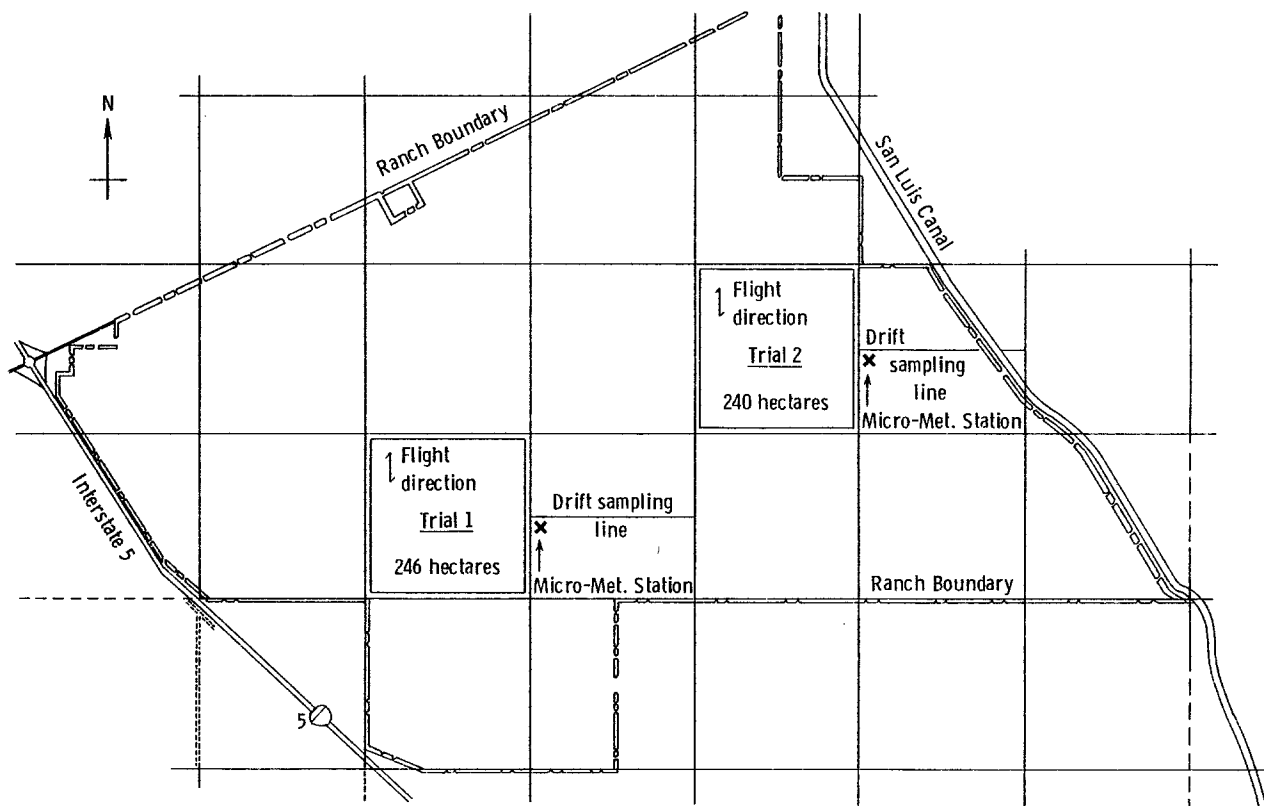


Fig. 1. Part of Telles Ranch, showing trials locations

addition to the air sampling procedures, drift fallout was assessed with four polyethylene sheets (15×45 cm) mounted on corkboards located at each station. These were placed at 10 m apart and parallel to the spray area perimeter. The outer two sheets were located at the height of the cotton, which was growing on either side of the road on which the stations were positioned. The inner two sheets were located at ground level on the road. All air sampler filters and fallout sheets were handled and stored in the manner previously described.

Operational Details: Figure 1 shows the two sites which were sprayed for cotton harvest aid. In the first trial, paraquat was used in combination with sodium chlorate (Tumbleleaf®) to open residual mature cotton bolls (Table 2). In the second trial, paraquat was used alone to open residual top bolls before harvesting. The application rate was one US pint Paraquat CI® in 10 US gal/water/A in both trials. This corresponded to a spray strength of 2.9 g/L. Sodium chlorate was applied at 3 to 4 lb in 10 US gal/water/A in the first trial. Mixing and loading of the chemicals was done with a 'closed-transfer' system. The aircraft, spray nozzles, and nozzle attitudes were identical in both trials.

A micro-meteorological station was located 25 m downwind from the spray application area along the drift line. The station consisted of a telescopic mast on which were mounted a Casella Sensitive Anemometer and windvane at 5 m height above ground level. Observations of average wind velocity and direction were recorded at several intervals before and during the trials. Measurements of air temperature and relative humidity were provided by a Weathermeasure® (Weathermeasure Corp, Sacramento, CA) chart-recorder located at ground level in the shade.

This provided a continuous readout of temperature and humidity throughout the trials.

Analysis of Paraquat: Dermal exposure pads and air sampler filters were extracted by soaking in a suitable volume of saturated ammonium chloride for an appropriate time (Table 3). A portion of each supernatant extract was, where necessary, clarified by filtration or centrifugation (glass fiber filters only at 3000 rpm for 10 min). A 10 ml aliquot was taken from each clarified extract and its paraquat content reduced to the free radical by treatment with 2 ml of 0.2% w/v sodium dithionite solution in 0.3 N sodium hydroxide solution. The Staplex TFA41 filters had been visibly contaminated with dust during air sampling, and these were subsequently re-extracted (including residual dust) using more rigorous conditions. 6M sulphuric acid (20 ml) was added to the samples which were boiled for 5 hr under reflux. The cooled samples were diluted to 100 ml with water, filtered through Celite 545®, and the filtrates allowed to percolate through columns each containing 5 g. Zerolit® ion exchange resin at a flow rate of 5 to 10 ml/min. The columns were washed at a flow rate of 3 to 4 ml/min successively with water, 2M hydrochloric acid, water, 2.5% (w/v) ammonium chloride solution, and water. The paraquat was eluted from the column with saturated ammonium chloride solution at a flow rate of about 1 ml/min. The first 50 ml was collected and 0.2% sodium dithionite solution was added. The absorbance spectra of all solutions were recorded with a Pye Unicam SP1800 spectrophotometer over the range 370 to 430 nm against saturated ammonium chloride, similarly treated with dithionite solution, in the reference beam. Where a peak was seen with an absorbance maximum at 390 nm,

Table 2. Operational Details

Trial	Crop	Area sprayed	Block number	Formulation sprayed	Application rate		Paraquat conc in tank (g/L)	Total amount of paraquat concentrate sprayed		Aircraft type and number used	Nozzle type, diameter and altitude
					US	SI		US gallons	Liters		
1	Cotton	607 acres or 246 hectares	17	Paraquat C1 + X-77 + Tumbleleaf ^a	1 pt PQ C1	1.2 liters PQ C1	2.9	76	288	Thrush Commander	D10 0.3 cm (1/8") horizontal
					1 pt X-77	1.2 liters X-77					
2	Cotton	593 acres or 240 hectares	10	Paraquat C1 + X-77	3-4 lbs Tumbleleaf in 94 liters water per acre	3.3-4.5 kg Tumbleleaf in 94 liters water per hectare	2.9	74	280	Thrush Commander	D10 0.3 cm (1/8") horizontal
					1 pt PQ C1	1.2 liters PQ C1					
					1 pt X-77 in 10 gals water per acre	1.2 liters X-77 in 94 liters water per hectare					

^a Sodium chlorate

a baseline was constructed as a tangent to the curve in the region of 410 nm to a point on the opposite slope corresponding to 390 nm. Concurrently with each batch of analyses, a calibration curve of peak height at 396 nm vs paraquat concentration ($\mu\text{g/ml}$) was prepared from standard paraquat solutions over a suitable concentration range, dependent on the estimated concentrations of the sample extracts. The concentrations of paraquat in the extracts were determined from the calibration curve and the total amount in the samples calculated.

The average recovery of the ammonium chloride extraction method was 100% (78 to 120%) and the limits of determination ranged from 0.03 to 10 μm /sample, depending on the sample type (Table 3). It was not possible to determine recoveries for the Staplex filters and dust extracted with sulphuric acid, but the average levels for this method are 80 to 95%.

Calculations

Dermal Exposure: Individual body part and total dermal exposure to paraquat were calculated by the method of Durham and Wolfe (1962). In addition, total dermal doses in terms of mg/kg/hr were estimated from skin exposure data, and from clothing penetration estimates.

Respiratory Exposure: Total and respirable paraquat concentrations in air were calculated from each worker's personal sampling data, using the instrument sampling rates and durations of exposure. The concentrations were expressed as μg paraquat/ m^3 air:

$$\text{paraquat}/\text{m}^3 = \frac{\mu\text{g paraquat}/\text{filter} \times 1000 (\text{l})}{\text{sampling rate (l/min)} \times \text{duration (min)}}$$

The respiratory minute volume (rmv) of females doing light work was used to calculate the paraquat concentrations in air from the face mask data. The rmv used was 16.4 L/min (Documenta Geigy 1972):

$$\mu\text{g paraquat}/\text{m}^3 = \frac{\mu\text{g paraquat}/\text{filter} \times 1000 (\text{l})}{\text{rmv (l/min)} \times \text{duration (min)}}$$

Paraquat Drift Sampling: Total and respirable paraquat concentrations in air were calculated from the amounts of paraquat collected by the Staplex Hi-Vol and Hexhlet® samplers at each sampling station, together with the instrument sampling rates and sampling durations:

$$\mu\text{g paraquat}/\text{m}^3 = \frac{\mu\text{g paraquat}/\text{filter} \times 1000 (\text{l})}{\text{sampling rate (l/min)} \times \text{duration (min)}}$$

For the first trial, an abrupt change in wind direction occurred after 70 min of sampling. The total sampling period was 130 min (100 min spraying time plus 30 min to collect residual airborne drift). Owing to the change in wind direction, after which the sampling efficiency was considerably reduced, a sampling period of 70 min was used for purposes of calculation. Particle size distributions were calculated for paraquat collected by the Andersen 2000 particle sizer located at each sampling station. The effective "cut off" diameters (ECD), theoretically 7.0, 3.3, 2.0 and 1.1 μm , were recalculated, as they are dependent upon the sampler flow rate; the figures are for an instrument operated at 560 L/min. In practice, it was not possible to maintain the instrument flow rates precisely at this level, and they varied between 476 and 588 L/min. The following equation (provided by

Andersen 2000 Inc) was used to recalculate the ECDs for each sampler:

$$\text{Dp50} = \frac{18\mu\psi N\pi Dc^3}{4C_p Q}$$

Where:

Dp50 = aerodynamic diameter particle size, cm (effective cut point), μ = Gas viscosity, poise = $[63 + .40T(^{\circ}\text{K})] \times 10^{-6} = 1.81 \times 10^{-4}$ at 70°F, ψ = Dimensionless inertial impaction parameter, 0.14, N = Number of jets per stage (300), $\pi = 3.14$, Dc = Jet diameter, cm, C = Cunningham slip correction factor, which is $\frac{1 + .165 \times 10^{-4}}{\text{Dp50}}$ for STP, P = Density of water, 1 gm/ cm^3 , Q = Actual flow rate, cm^3/sec .

The data are presented as percentage of total mass of paraquat droplets within the size ranges, and cumulative percentages less than the quoted size ranges.

Results

Meteorological Measurements

Air temperature throughout the two trials varied between 22 and 29.5°C and increased as the trials progressed (Table 4). Relative humidity fell sharply after 8.00 hr during the first trial from 66% to 32% by 10.00 hr and during the second trial from 50% at 7.00 hr to 30% by 10.00 hr. Wind velocity varied very little during the trials, and remained below the maximum permitted speed of 4.5 m/sec throughout (Fresno County (California) Department of Agriculture, Cotton Harvest Aid Uses 1979).

Wind direction was monitored on three days prior to the trials, at approximately the same time that the trials were due to start; 6.00 to 8.00 hr. The pattern that emerged was a westerly wind, which gradually moved round through north-west to north, in a clockwise manner. For the first 70 min of the first trial, the direction was fairly constant at west south-west, with gusting from the south-west. Afterwards, there was an abrupt change to north, north-west. For the drift sampling calculations, a sampling duration of 70 min was used because of this change. During the second trial, direction was constant throughout, from west, south-west. By 9.30 hr, the direction had moved clockwise with the result that the wind was northerly, with slight gusting from the north-west.

Dermal Exposure

Total dermal exposure and dose calculations were based on "exposed body part" and "exposure beneath clothing" measurements. Flagger 1 received the highest exposure in both trials of 2.39 and 1.05

Table 3. Extraction Conditions, Limits of Determination and Recovery Factors for Each Sampling Medium

Sample	Extraction volume (ml)	Extraction time (min)	Limit of determination ($\mu\text{g}/\text{sample}$)	Mean recovery (% \pm SD)
25 cm ² body pads	12	15	0.10	98 \pm 16 (11)
Personal air sampler filters	12	15	0.03	91 (2)
Staplex filters	12	15	0.05	105 (2)
Hexhlet filters	12	15	0.05	120 (2)
Andersen filters	100	15	0.10	106 \pm 13 (8)
Gloves	100	60	0.50	90 (2)
Tubigrip	500	60	10.00 ^a	78 (2)
T-shirts	500	60	10.00	106 (2)
Face masks	50	60	not applicable ^b	—
Fallout sheets	100	15	0.30	106 (4)

Figures in parentheses are the number of determinations conducted

^a This relatively high limit of determination was due to an intrinsically high background in extracts of Tubigrip

^b Only 2 samples obtained, both of which contained relatively high amounts of paraquat. Therefore a limit of determination was unnecessary

Table 4. Meteorological Measurements

Trial	Time (hr)	Air temperature (°C)	Relative humidity (%)	Time (hr)	Wind-velocity (m/s)	Direction
1	08.00	18.0	66	05.00	6.34	WSW to SW
	09.00	26.5	43	08.08	2.60	
	10.00	29.5	32	08.45	2.50	
				10.05	3.13	
				mean =	3.64	NNW
2	07.00	18.0	50	07.20	2.00	WSW
	08.00	26.0	28	08.25	1.68	WSW
	09.00	24.0	32	09.30	1.23	W
	10.00	26.5	30		mean =	1.64

mg paraquat/hr (Table 5), Pilot 2 received the lowest exposure in both trials of 0.05 mg paraquat/hr. The dermal exposure of the mixer-loader was also consistent at 0.18 and 0.2 mg paraquat/hr. Pilot 1 did not wear his normal shirt over the sample T-shirt given to him for the first trial; therefore, the quantity of paraquat detected in this T-shirt (0.01 mg paraquat/hr) was not used in the calculation of total dermal exposure and dose.

Respiratory Exposure

The concentrations of total paraquat in the breathing zone ranged from $<0.1 \mu\text{g}/\text{m}^3$ to $26.3 \mu\text{g}/\text{m}^3$ for flagger 1, trial 1 (Table 6). No respirable paraquat was measured for any worker.

Paraquat Drift

Two sets of data for total airborne paraquat concentrations are given (Table 7) to illustrate the dif-

ferences in paraquat concentration according to the method of extraction. Paraquat drift concentrations were higher for both total and respirable paraquat in trial 2 relative to trial 1, and decreased with distance downwind from site of application. Figure 2 illustrates the drift profiles for total airborne paraquat for both trials, to 800 m downwind, and shows a more rapid decrease in drift concentration during trial 1. The highest concentration of total paraquat measured was $16.7 \mu\text{g}/\text{m}^3$ at 50 m during trial 2. This was nearly 3 times the highest concentration measured in trial 1 ($6.4 \mu\text{g}/\text{m}^3$ at 50 m). The highest concentration of respirable paraquat ($0.15 \mu\text{g}/\text{m}^3$) was also measured at 50 m in trial 2. The drift fallout (Table 8, and Figure 3) follows the same trend, with relatively much larger amounts of paraquat falling out at 50 and 100 m, compared to 200 to 1600 m. Generally, the higher airborne drift concentrations measured in trial 2 were complemented by correspondingly higher fallout concentrations. The particle size distribution data (Table 9) show general agreement with the trends demonstrated for total and respirable paraquat in Table 7. In trial 1,

Table 5. Dermal Exposure to Paraquat

Trial	Personnel	Dermal exposure (mg PQ/hr)											Total exposure (from exposed body part and exposure beneath clothing determinations)	Dermal dose (mg PQ/kg/hr)	
		Clothed body parts					Exposed body parts								Exposed beneath clothing
		Back	Forearms	Thighs	Lower legs	Abdomen	Head	V of neck	Top of shoulders	Back of neck	Hands	Trunk	Legs		
1	Flagger 1	0.44	0.40	1.30	0.60	2.80	1.40	0.11	0.33	0.03	0.32	0.20	ND ^a	2.39	0.04
	Flagger 2	0.21	0.04	0.08	0.02	0.001	0.05	0.001	0.01	0.004	0.02	0.01	ND	0.10	1.7×10^{-3}
2	Mixer/Loader	NA ^b	14:30 (Up Arm)	8:35	NA	NA	ND	0.07	NA	0.01	NA	0.04	0.06	0.18	2.6×10^{-3}
	Pilot 1	ND	ND	ND	ND	NA	ND	ND	ND	ND	0.07	0.01 ^c	0.03	0.10	1.4×10^{-3}
	Pilot 2	ND	ND	ND	0.05	NA	ND	ND	ND	ND	0.04	0.01	ND	0.05	7.1×10^{-4}
	Flagger 1	0.34	0.84	10.8	4.00	10.89	0.10	0.44	0.03	0.01	0.40	0.07	ND	1.05	0.02
	Flagger 2	Pad	0.30	0.5	0.15	0.37	0.04	0.02	0.03	0.02	0.02	0.06	ND	0.19	3.2×10^{-3}
		mis-laid (Up Arm)													
	Mixer/Loader	NA	ND	0.1	NA	NA	ND	ND	NA	ND	NA	0.15	0.05	0.20	2.9×10^{-3}
	Pilot 1	ND	ND	ND	ND	NA	ND	ND	ND	ND	0.20	0.04	0.02	0.26	3.7×10^{-3}
	Pilot 2	ND	ND	ND	ND	NA	ND	ND	ND	ND	0.02	0.01	0.02	0.05	7.1×10^{-4}

^a ND = None detected, limits of determination: exposure pads 0.1 µg/sample; gloves 0.5 µg/sample; Tubigrip and T-shirt 10 µg/sample

^b NA = None applied

^c = Not included in calculation of total exposure (see text)

Table 6. Respiratory Exposure to Paraquat

Trial	Personnel	Sampling duration (min)	Total volume of air sampled for total paraquat determination (1)	Airborne concentration of total paraquat ($\mu\text{g}/\text{m}^3$)	Total volume of air sampled for respirable paraquat determination (1)	Airborne concentration of respirable paraquat ($\mu\text{g}/\text{m}^3$)
1	Flagger 1	100	300	26.3	190	ND ^a
	Flagger 2	100	300	ND	190	ND
	Mixer/Loader	137	411	0.1	260	ND
	Pilot 1	100	^b	—	190	ND
	Pilot 2	100	300	ND	190	ND
2	Flagger 1	75	262.5	ND (facemask 76.4)	142.5	ND
	Flagger 2	75	262.5	2.80 (facemask 25.2)	142.5	ND
	Mixer/Loader	105	367.5	0.11	199.5	ND
	Pilot 1	75	262.5	ND	142.5	ND
	Pilot 2	75	262.5	0.34	142.5	ND

^a ND = None detected, limit of determination 0.03 $\mu\text{g}/\text{filter}$

^b = Pump failure

Table 7. Paraquat Drift Concentrations

Sampling station	Dis- tance down- wind (m)	Total airborne concentration ($\mu\text{g}/\text{m}^3$) ^c						Respirable airborne concentration ($\mu\text{g}/\text{m}^3$)			
		Trial 1		Trial 2		Trial 1		Trial 2			
		Volume of air sampled (m ³)	Concentration	Volume of air sampled (m ³)	Concentration	Volume of air sampled (m ³)	Concentration	Volume of air sampled (m ³)	Concentration		
1	50	27.65	3.54	6.40	39.5	11.14	16.66	3.5	1.4×10^{-2}	5.0	0.15
2	100	27.65	0.65	2.68	39.5	8.10	12.91	3.5	ND ^a	5.0	0.13
3	200	27.65	0.03	2.10	NS ^b	—	—	3.5	ND	NS	—
4	400	31.15	9.3×10^{-3}	0.81	44.5	1.58	5.85	3.5	1.4×10^{-2}	5.0	0.12
5	800	27.65	1.8×10^{-3}	3.44	39.5	0.99	4.03	3.5	ND	5.0	3.6×10^{-2}
6	1600	31.15	ND	1.70	44.5	1.34×10^{-3}	0.47	NS	—	5.0	1.4×10^{-2}
ML		NS			Unknown			NS		NS	

^a ND = None detected (limit of determination = 0.05 $\mu\text{g}/\text{sample}$)

^b NS = No sampling

^c { 1 = Calculated from ammonium chloride extraction data only
2 = Calculated from both ammonium chloride and 6M sulphuric acid extraction data

no paraquat was detectable beyond Station 4 (400 m). At Station 1 (50 m) 98.2% of spray droplets were $>7.1 \mu\text{m}$ diameter. 1.8% were within the range 2.0 to 3.4 μm . At stations 2 and 3 (100 and 200m), all droplets were >7.2 and 6.9 μm . In trial 2 $>98\%$ of droplets were $>7 \mu\text{m}$ diameter at all stations.

Discussion and Conclusions

These worker exposure and drift hazard evaluation studies were conducted during commercial aerial

applications of paraquat to cotton, as part of the annual cotton harvest aid program in the San Joaquin Valley of California. The exposure and drift data are representative examples of likely exposure and drift potential under the prevailing meteorological and operating conditions, which were within the limits set by the Fresno County, California, Department of Agriculture, Cotton Harvest Aid Uses (1979).

The dermal and respiratory exposures measured in the two trials were extremely low for all workers,

in comparison with exposures determined during hand-held application of paraquat (Chester and Woollen 1982). Flagger 1, trial 1 was the most highly exposed worker and her combined *potential* dermal and respiratory exposure was calculated to represent 2.42 (2.39 + 0.03) mg/hr, or 19.36 mg/8 hr working day, which is a dose of 0.32 mg/kg/day. Her *potential* respiratory exposure therefore contributed about 1% to her combined exposure, which is in accordance with previously published studies of the exposure of aerial applicators and ground crews (Jegier 1964; Wolfe *et al* 1967; Richter *et al* 1980). The significance of the level of dermal exposure measured for the flagger can best be assessed by consideration of the percutaneous absorption of paraquat. The rate of paraquat absorption across human whole skin preparations *in vitro* is exceedingly slow (Dugard P H, ICI Central Toxicology Laboratory, personal communication). The total absorption of paraquat dichloride from aqueous spray strength dilutions (5g/L) of formulations following 24 to 30 hr contact was 0.52 $\mu\text{g}/\text{cm}^2$ of skin. Subsequent absorption (between 24 to 30 and 45 to 53 hr periods during contact) occurred at rates less than 0.1 μg paraquat dichloride/ cm^2/hr . The exposed skin contamination of the flagger (2.39 mg/hr or 19.12 mg/8 hr working day) is equivalent to a spray dilution volume of 6.6 ml which was distributed over a skin surface area of 9,424 cm^2 , (World Health Organization 1982). If the distribution of this spray was even, then the contamination was equivalent to 0.70 $\mu\text{l}/\text{cm}^2$, or 2.03 μg paraquat/ cm^2 after 8 hr. From Dugard's work, 0.14 $\mu\text{g}/\text{cm}^2$ paraquat is likely to be absorbed over 8 hr, (0.52/30 \times 8), if all paraquat is present at time zero. Therefore, about 7% of the paraquat dermal contamination of flagger 1 would have been absorbed if evenly distributed. This is perhaps an over-estimation, since the nature of the contamination was probably random splashes over a relatively small area of exposed skin, in which case the absorption kinetics would have been saturated to an even greater extent, resulting in a lower total absorption than that calculated above.

NIOSH/OSHA (1981) quote a Threshold Limit Value (TLV) for *total* paraquat of 500 $\mu\text{g}/\text{m}^3$ and the American Conference of Governmental Industrial Hygienists (Anon 1983) have published a TLV (Time Weighted Average) for *respirable* paraquat in the air of the workroom, which is 100 $\mu\text{g}/\text{m}^3$. TLV's have not been established for agricultural workers, working in the open air. Agricultural spraying operations of the type studied may involve relatively high intermittent excursions above and below the "average" concentrations determined in this study. Aerial applicators (pilots) and groundcrew are not

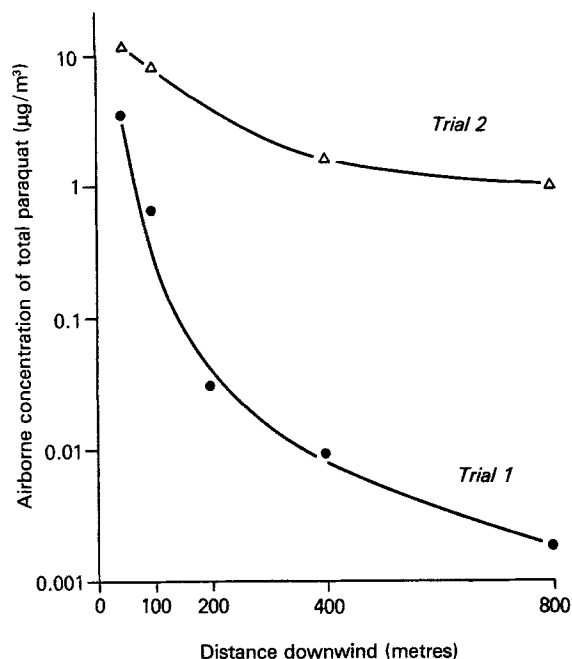


Fig. 2. Airborne concentration of total paraquat drift to 800m downwind

exposed continually for eight hours per day and forty hours per week, but their exposure is confined to short periods of 10–15 min, alternating with periods of nil or negligible exposure of similar duration. With this limitation in mind, the highest concentration of *total* paraquat recorded in the present trials was 26.3 $\mu\text{g}/\text{m}^3$ for flagger 1 in trial 1, which is lower than the TLV for total paraquat. This concentration extrapolates to an exposure to total paraquat of 207 $\mu\text{g}/8$ hr using a respiratory minute volume of 16.4 L/min for females doing light work (Documenta Geigy 1972). This is a factor of 19 less than the amount potentially available for inhalation (3.9 mg/8 hr) at the TLV of 500 $\mu\text{g}/\text{m}^3$. From the facemask contamination data for flaggers in trial 2, the highest hypothetical total paraquat concentration was 76.4 $\mu\text{g}/\text{m}^3$ which is a factor of 7 less than the TLV for total paraquat. This may have been comprised both of droplets trapped on the mask covering the nasopharyngeal region by both inspiration of paraquat-laden air and direct impingement of large, non-respirable droplets sprayed by the aircraft passing overhead. At the mixing-loading area in trial 2, no airborne paraquat was detected by a Staplex Hi-Vol sampler and an Andersen 2000 particle sizing sampler, located at head height on the downwind side. The sampling efficiency of these instruments was considerably reduced by the vast amounts of dust generated by the aircraft taking off

Table 8. Paraquat Drift Fallout

Drift sampling station	Distance downwind (m)	Paraquat drift fallout ($\mu\text{g paraquat/m}^2$) ^a			
		Sheet	Trial 1	Sheet	Trial 2
1	50	1	78.5	1	385.5
		2	45.9	2	93.3
		3	251.9	3	281.5
		4	311.0	4	385.2
		Mean	171.9	Mean	286.3
		SD	129.6	SD	137.6
2	100	1	9.04	1	207.4
		2	<4.4	2	31.1
		3	34.1	3	177.8
		4	444.4	4	81.5
		Mean	123.0	Mean	124.4
		SD		SD	82.2
3	200	1	13.8		
		2	<4.4		
		3	<4.4	No samples taken	
		4	<4.4		
		Mean	6.7		
		SD			
4	400	1	<4.4	1	20.74
		2	<4.4	2	<4.4
		3	<4.4	3	<4.4
		4	32.6	4	37.0
		Mean	11.5	Mean	16.6
		SD		SD	
5	800	1	<4.4	1	25.2
		2	<4.4	2	<4.4
		3	<4.4	3	11.0
		4	<4.4	4	5.5
		Mean	<4.4	Mean	11.5
		SD		SD	
6	1600	1	<4.4	1	4.7
		2	<4.4	2	5.5
		3	<4.4	3	<4.4
		4	<4.4	4	<4.4
		Mean	<4.4	Mean	4.8
		SD		SD	

^a Limit of determination – 0.3 $\mu\text{g/sample}$

Values less than the limit of determination are included in calculation of mean as detectable, but nonquantifiable, paraquat was present in some samples

and landing and subsequently “choking” the filters of the samplers, thus reducing the flow rates and rendering the volume of air sampled unknown. A total of 14 μg paraquat were detected following re-extraction of the total Staplex Hi-Vol sample and 9 μg were extracted from 0.1 g of dust which was ‘loose’ in the polyethylene bag containing the sampler filter. The mixing-loading site was located over two miles away to the south-west of trial 2 location and in an ‘open’ area in which no cotton was grown or paraquat sprayed at that time. In conclusion, the levels of dermal and respiratory exposure of the three occupational groups determined in the two trials of this study do not represent a significant toxic hazard.

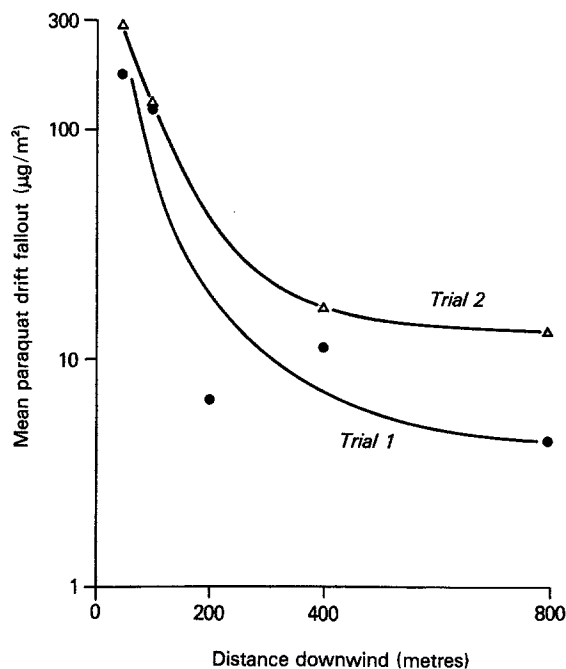


Fig. 3. Decrease in mean paraquat drift fallout to 800m downwind

If the airborne concentration data from the two trials are compared, it is seen that levels were higher in trial 2 at all sampling stations. This is attributed to variation of the wind direction, which was a particular problem in the first trial. The paraquat fallout data, however, are similar for both trials down to Station 4 (400 m downwind). The data of the second trial give more accurate estimates of drift, because the wind direction was much more stable at west south-west to west, and so more in line with the sampling stations located due east of the application site. During the first trial, there was directional variation from west south-west to south-west and then an abrupt change to north, north-west after 70 min of sampling. Owing to this variation, the paraquat drift probably bypassed the 1600 m sampling station. The respective mean wind speeds indicate that paraquat sprayed at the further end of the fields from the sampling stations would have reached Station 6 (1600 m) in 14 and 32 min in trials 1 and 2 respectively. Therefore, we are confident that all potentially available airborne paraquat would have been sampled.

The measurements of drift demonstrated decreases in the total and respirable concentrations of paraquat with increasing distance downwind from the site of application (Table 7). Two sets of data for the total concentrations are given, based on two

Table 9. Particle Size Distributions of Paraquat Drift

Station	Distance downwind (m)	Paraquat particle size distributions						
		Trial 1			Trial 2			
		Particle size diameter (μm)	% in size range	Cumulative % less than	Particle size diameter (μm)		% in size range	Cumulative % less than
	Initial	Final						
1	50	>7.1	98.2	1.8	>7.1	>8.2	99	1
		3.4-7.1	ND ^a	1.8	3.3-7.1	3.8-8.2	1	0
		2.0-3.4	1.8	0	2.0-3.3	2.3-3.8	ND	
		1.1-2.0	ND		1.1-2.0	1.3-2.3	ND	
		<1.1	ND		<1.1	<1.3	ND	
2	100	>7.2	100.0	0	>7.4	>8.3	99.05	0.95
		3.4-7.2	ND		3.5-7.4	3.9-8.3	0.9	0.05
		2.1-3.4		2.1-3.5	2.4-3.9	ND	0.05	
		1.2-2.1		1.2-2.1	1.3-2.4	0.05	0	
		<1.1		<1.2	<1.3	ND		
3	200	>6.9	100.0	0	No samples taken			
		3.3-6.9	ND					
		2.0-3.3	ND					
		1.1-2.0	ND					
		<1.1	ND					
4	400	>7.0	ND		>6.8	>7.1	98.04	1.96
		3.3-7.0	100.0		3.2-6.8	3.3-7.1	0.49	1.47
		2.0-3.3	ND		1.9-3.2	2.0-3.3	0.16	1.31
		1.1-2.0		1.1-1.9	1.1-2.0	0.65	0.65	
		<1.1		<1.1	<1.1	0.65	0.00	
>7.7	>7.3	>7.6		98.2	1.80			
5	800	3.7-7.7	ND		3.4-7.3	3.6-7.6	1.05	0.75
		2.2-3.7		2.1-3.4	2.2-3.6	ND	0.75	
		1.2-2.2		1.2-2.1	1.2-2.2	0.75	0.00	
		<1.2		<1.2	<1.2	ND		
		>7.2		>7.1	>7.1	100.0	0.00	
6	1600	3.4-7.2	ND		3.4-7.1	3.4-7.1	ND	
		2.1-3.4		2.0-3.4	2.1-3.4	ND		
		1.1-2.1		1.1-2.0	1.1-2.1	ND		
		>1.1		<1.1	<1.1	ND		
				>7.1				
Mixing/loading area		No samples taken		3.4-7.1	No readings obtainable	ND		
				2.0-3.4				
				1.1-2.0				
				<1.1				

^a ND = None determined (limit of determination 0.1 $\mu\text{g}/\text{sample}$)

different extractions of the same samples. At the time of analysis, it was observed that the Staplex Hi-Vol air sampler filters were visibly contaminated with dust. This excess dust was generated at the time of the trials by our motor vehicles being driven along the track on which were located the sampling stations.

Re-extraction of the Hi-Vol filters demonstrated similar levels of paraquat at all stations in the same trial, with the exception of Station 6 sample, trial 2. This station was located on the other side of a raised canal (Figure 1) in an area not directly sprayed with paraquat. These data do not

show the typical drift decay curve with increasing distance downwind. The soil-bound paraquat was derived from either the free, airborne component, or was already soil-bound from previous paraquat applications. For the purposes of comparison with the TLV, we must use the 'worst case' exposure, and assume that all extracted paraquat was airborne and biologically available. From these data, the highest concentration of paraquat was 16.7 $\mu\text{g}/\text{m}^3$ at Station 1 (50 m) in trial 2, which may be compared to 11.1 $\mu\text{g}/\text{m}^3$ calculated for a sample extracted with ammonium chloride.

The drift concentrations determined in this study

may be compared with those reported by Seiber and Woodrow (1981) who used similar air sampling equipment to obtain 'extrapolated interval average' values of 4.31 and 10.7 $\mu\text{g}/\text{m}^3$ at the 1 m downwind edge. The concentrations decreased with distance downwind to $<0.05 \mu\text{g}/\text{m}^3$ at about 400 m. Despite a three-fold higher application rate, the concentrations determined in our study are considerably higher at greater distances downwind. At 50 m, the highest concentration reported by Seiber and Woodrow was about $0.1 \mu\text{g}/\text{m}^3$, which is much lower than $16.7 \mu\text{g}/\text{m}^3$ measured at 50 meters in our study. Various factors could contribute to these differences, notable among which are the absence of a drift control agent such as Nalco-trol in our formulations, and the differing meteorological conditions and application equipment. The decrease in concentration in our trials was quite rapid, with only minute levels detected beyond 100 m. This is in accordance with Seiber and Woodrow's work.

The particle size distribution data (Table 9) demonstrate that only small percentages of droplets were within the respirable range at all stations. The highest percentage of respirable droplets was 1.96%, measured at Station 4 (400 m) in trial 2. No firm trend can be established for these data, in terms of relating proportion of respirable droplets to distance downwind. However, it is emphasized that 1.96% of the total amount of paraquat collected represents only 1.2 μg (based on estimates below the limit of determination). The highest amount of respirable paraquat collected was 1.8 μg at Stations 1 and 2, trial 2, which represented 1 and 0.95% of the totals collected. These data follow the trend established for the total and respirable airborne paraquat concentrations, i.e., decreasing concentration, or amount, with increasing distance downwind from the site of application.

In interpreting the paraquat drift hazard to individuals standing downwind of an aerial application of paraquat to cotton, a comparison with the TLV is drawn. However it is again recognized that this may not be strictly appropriate for the agricultural workplace because the concentration of a spray cloud drifting downwind is variable, and is unlikely to be present for eight hours a day and five days a week. In addition, cotton defoliation is spread over a few weeks only during the late summer. The highest concentration of respirable paraquat was measured at 50 m during trial 2 ($0.15 \mu\text{g}/\text{m}^3$), which is equivalent to 2.06 $\mu\text{g}/8\text{hr}$ for a male doing light work (respiratory minute volume 28.6 L/min, Documenta Geigy 1972). This is less than the amount available for inhalation (1.37 mg/8hr) at the TLV of

100 $\mu\text{g}/\text{m}^3$. The highest total paraquat concentration of $16.7 \mu\text{g}/\text{m}^3$ is equivalent to an exposure of 229 $\mu\text{g}/8\text{hr}$ for a male doing light work. This is less than the amount potentially available for inhalation (6.86 mg/8hr) at the TLV of 500 $\mu\text{g}/\text{m}^3$. These determinations of the concentrations of paraquat in air to a distance of 1600 m downwind lead to the conclusion that there is no evidence for a respiratory toxicity hazard as a consequence of aerial application.

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References

- Akesson NB, Yates WE, Cowden RE (1977). Procedures for evaluating the potential losses during and following pesticide application. Paper No 77-1504 presented at the 1977 Winter Meeting of the American Society of Agricultural Engineers, Chicago, Illinois
- Andersen 2000 Inc (1976). Operating manual for high volume particle sizing samplers. Andersen 2000 Inc, Atlanta, Georgia
- Anonymous (1983). Threshold limit values for chemical substances and physical agents in the workroom environment with intended changes for 1983-4. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio
- Chester G, Woollen BH (1982). Studies of the occupational exposure of Malaysian plantation workers to paraquat. *Brit J Ind Med* 39:23-33
- Documenta Geigy (1972) Scientific Tables. 7th edn. Diem K and Lentner C (ed). Ciba Geigy Limited, Basle, Switzerland
- Durham WF, Wolfe HR (1962). Measurement of exposure of workers to pesticides. *Bull World Health Org* 26:75-91
- Fresno County (California) Department of Agriculture (1979). Cotton harvest aid uses. Sacramento, California
- Hogarty C (1975). Exposure of spray operators to paraquat. Institute for Industrial Research and Standards, Dublin, Ireland
- Jegier Z (1964). Health hazards in insecticide spraying of crops. *Arch Environ Health* 8:670-674
- NIOSH/OSHA (1981). Occupational health guidelines for chemical hazard—paraquat. January. U.S. Department of Health and Human Services, Washington, DC
- Orenstein AJ (1960) ed. Recommendations P619. Proc Pneumoconiosis. Conf. Univ of Witwatersrand, Johannesburg, South Africa 1959. J A Churchill, London
- Richter ED, Cohen B, Livia M, Schoenberg J, Weisenberg E, Gordon M (1980). Exposure of aerial spray workers to paraquat. *Isr J Med Sci* 16:96-100
- Seiber JN, Woodrow JE (1981). Sampling and analysis of airborne residues of paraquat in treated cotton field environments. *Arch Environ Contam Toxicol* 10:133-149
- Staff DC, Comer SW, Armstrong JS, Wolfe HR (1975). Expo-

- sure to the herbicide paraquat. *Bull Environ Contam Toxicol* 14:334-340
- Swan AAB (1969). Exposure of spray operators to paraquat. *Brit J Ind Med* 26:322-329
- Wojeck GA, Price JF, Nigg HN, Stamper JH (1983). Worker exposure to paraquat and diquat. *Arch Environ Contam Toxicol* 12:65-70
- Wolfe HR, Durham WF, Armstrong JF (1967). Exposure of workers to pesticides. *Arch Environ Health* 14:622-633
- World Health Organization* (1982). Field surveys of exposure to pesticides. Standard Protocol, VBC/82.1. Division of Vector Biology and Control, Geneva, Switzerland
- Yates WE, Akesson NB, Coutts HH (1966). Evaluation of drift residues from aerial applications. *Trans ASAE* 9:389-393, 397
- Yates WE, Akesson NB, Cowden RE (1974). Criteria for minimizing drift residues on crops downwind from aerial applications. *Trans ASAE* 17:627-632

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